PB-216 865

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May 1970

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COAL MINE DRAINAGE RESEARCH

Chairman, C. T. Holland

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DISPOSAL OF CHEMICAL SLUDGES AND BRINES

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INTRODUCTION

Coal mine drainage is a dilute solution of salts, frequently acidic and containing iron and sulfate ions. At one extreme it strongly resembles pickling acid wastes from steel mills while at the other extreme it is indistinguishable from good spring water. Good spring water is not a pollutant, of course, and can be allowed to run into the natural drainage. Mine drainage containing acids and iron salts may have to be treated to remove these pollutants so that the water which continues to flow from the mines may be released. Removal of the pollutants turns out to be only half of the problem. Disposal of the concentrated brines and sludges containing the polluting substances is at least as difficult as removing the pollutants in the first place.

Table I shows comparative data on the principal pollutants in two mine waters and the two acid waste streams from a typical steel mill (Maneval, 1966; FWPCA, 1968). There is a strong resemblance between the composition of water used to rinse pickled steel and a strong mine drainage. Since steel pickle liquors have long been recognized as a significant pollutant, one ought to be able to apply technology already developed for their disposal to mine wastes. The first difficulty, of course, is that the volume to be treated from a mine is much greater in respect to the value of the product than from a steel mill.

Table I

Comparative Analyses
mg/l or ppm

	Mine Drainage (Maneval 1966)		"Typical" Steel Mill Pickle Liquors (FWPCA 1968)	
	Morea (strip pit)	Marianna (bore hole)	Rinse Water	Strong Liquor
Acidity as $CaCO_3$ or H_2SO_4	190	4,040	3,000	38,000
Fe	6	815	4,100	52,000
SO_4	290	10,000	10,800	125,000
pH	3.2	2.6	less than 2.0	

The other difficulty is that economical disposal of steel mill wastes is even today considered to be an unsolved problem. Nemerow (1963) says, "The treatment of pickling liquor is a problem of considerable magnitude. For most small steel plants the recovery of by-products from waste pickling liquor is not economically feasible and therefore they neutralize the liquor with lime.. Neutralization of pickle liquor waste with lime is costly because there is no salable end product and because there is a voluminous slow-settling sludge which is difficult to dispose of." Gurnham (1965) says, "The principal disadvantages of lime neutralisation are high cost and land area necessary to lagoon the neutralized slurry, which is equal in volume to that of the pickling solution plus the lime slurry. The slurry from conventional lime neutralization cannot be dewatered effectively

but remains plastic for a long time. Lime neutralization with controlled air oxidation of precipitated iron produces a more compact slurry which can be dewatered, requiring much less land for lagoons. High calcium lime is usually used for neutralization although other alkaline agents such as dolomitic lime, limestone, carbide sludge, and spent cleaning solutions can be used." Regarding the production of copperas ($FeSO_4.7H_2O$) as a salable product, he further says, "The commercial production of copperas provides only a partial answer to the disposal problem, as 5% of the steel industry's potential output completely satisfies the market demand." Pickle liquor is being considered as an additive in sewage treatment to remove phosphates. This use might take care of a fraction of mine waste concentrates in some areas.

Recently there has been a shift in pickling technology toward the use of HCl instead of H_2SO_4 because the HCl can be recovered. While this may cut the Gordion knot for the steel industry, it offers little consolation to those working on the mine waste problem since there is no way to convert pyrites to a more tractable chemical.

The drainage water from most mines is dilute and contains 100 or more pounds of water per pound of pollutant. Since the pollutants in unoxidized waters are quite soluble, most of this water in principle can be removed by distillation or reverse osmosis before the salts form precipitates and scale on the equipment. A concentration ratio of tenfold is reasonable for either process. The result would be 9 million gallons of reusable water and 1 million gallons of concentrated acidic brine for each 10 million gallons of waste. The recovered water might be sold but probably not for enough to pay the cost of separation. The one million gallons of concentrate must still be disposed. It will contain up to 50 tons of salts and acid which have no more value than strong pickle liquor which, as we have seen, is not a profitable item.

The water content of the waste brines and sludges accounts for a large fraction of the cost of disposal even after the wastes have been concentrated. The water contributes up to 90% of the haulage costs and will occupy over 80% of the volume of waste disposal lagoons or cavities. If the wastes are not concentrated before chemical neutralization, the water content can contribute up to 99% of the costs of hauling and storage. There is, of course, some advantage to transporting wastes as liquids in pipelines rather than by truck and freight train, but the fact remains that the water content of the wastes represents the largest fraction of the ultimate costs of disposal. Mines are cavities which could be used for ultimate disposal of waste solids but, unfortunately, they are not tight enough to retain water. If we can convert the soluble wastes to insoluble forms and separate them from the excess water, storage of the solid wastes should be a relatively easy problem. The main purpose of this paper is to discuss the problems of separating solids from water and to review some of the methods used in other fields to dispose of solid wastes.

Precipitation and Flocculation

The formation of solid precipitates from soluble salts is an attractive way to remove these soluble impurities from wastewater. The reaction of lime with acid mine wastes appears to be fairly simple. Acids are neutralized, iron hydroxide and calcium sulfate are precipitated as solids and H_2O is the product. Unfortunately, there are difficulties all along the way.

The Encyclopedia of Chemical Technology (Kirk and Othmer, 1948) says: "Although calcium sulfate is usually considered to be a simple compound, this is far from being the case. This substance is probably the subject of more confused and discordant statements, misinterpretation, and persistent lack of exact

information than any other compound in the category of inorganic materials. The multiplicity of known and postulated forms...and the range of their usefulness have engaged the interests and intensive study of many of the best scientists and technologists for nearly two hundred years, and yet the most recent writers recognize that uncertainties still exist."

In addition, calcium sulfate is quite soluble. A saturated solution of gypsum $CaSO_4 \cdot 2H_2O$ contains about 15,000 mg/l of sulfate, a concentration which will not be acceptable in many waters. Worse than this is the fact that the precipitate forms very slowly and tends to come out on nuclei attached to surfaces. This produces an adherent scale that can clog pipes in less than one day. There are many examples in the chemical literature of this perverse behavior of calcium sulfate. Some of the basic studies have been done on plaster of paris, the hemihydrate, $CaSO_4 \cdot 1/2H_2O$. When added to water this form of calcium sulfate dissolves and recrystallizes as gypsum. A large number of substances are known to retard the setting of plaster which means retarding the crystallization of gypsum. Glue and related colloids are among the best retarding substances but organic acids and slimes that may be present in some mine waters can also be expected to retard precipitation.

The formation of a new crystal in a liquid is inhibited by surface forces and large degrees of supersaturation are normally required to initiate growth. Once started, growth proceeds at a rate limited by the diffusion of molecules to the surface and by the presence of other substances which compete for surface sites. It is common practice to provide nuclei for crystal growth. One way to do this is to recycle sludge to the neutralizing basin or to use an upflow sludge blanket clarifier. In the sugar industry crushed crystals of purified sugar are used to initiate crystallization. Crystals as they grow accumulate a coating of impurities which inhibit further growth. It might be desirable to investigate mechanical fracturing of recycled gypsum sludge to control unwanted scale in neutralization equipment.

There have been several Office of Saline Water attempts to control scale in sea water evaporators by circulating seeds of calcium sulfate (Lu et al., 1969; McCutchan et al., 1969). The objective is to provide more surface area as suspended nuclei than solid surface in the boiler. The size of crystals in a precipitate is also controlled by the concentration of the reactants. At high concentrations crystal nuclei are formed spontaneously and rapidly. A large number of crystals means that each one will be small and the resultant precipitate will settle slowly and be difficult to dewater. A set of classical experiments by Von Weymann showed that barium sulfate which is normally difficult to filter could be precipitated as needle-like crystals at very low concentrations or as an amorphous gel at very high concentrations of the reactants (Nielsen, 1964; Hartman, 1947).

It has been observed that sludge formed from powdered limestone and waste acid is denser and settles better than sludge formed from calcium hydroxide (Hill, 1968). The latter is quite soluble and provides a high local concentration of calcium ions which forms large numbers of very small crystals of calcium sulfate. When limestone is used each particle is covered with an adherent coating of gypsum which limits diffusion of calcium ions and reduces the supersaturation. Undissolved limestone probably weights the precipitate and makes it settle faster and also provides a structure favorable to filtration. Thus, although limestone may be inefficient on a chemical basis when compared with slaked lime, it may be more efficient on an overall basis when the costs of thickening and disposal are included.

When ferric ions are neutralized they form a gelatinous precipitate that is difficult to filter. The precipitate forms flocs which adsorb suspended solids and clarify the water as they settle. When ferrous ions are neutralized and allowed to oxidize slowly by reaction with dissolved oxygen, the precipitate forms

very poor flocs and is difficult to remove. Because ferric ions are produced slowly one would expect larger crystals to be formed. This may be the case since the formation of flocs of inorganic hydroxides usually involves extremely minute crystals. Larger crystals formed slowly by oxidation of ferrous ions produce poorer flocs but the crystals are still much too small to be filtered.

Floc formation is aided by additions of colloidal flocculants. Most commercial flocculants are water soluble polymers carrying bound ions which may be either positive or negative. Together with their counter ions these polymers are thus electrolytes and are usually known as polyelectrolytes although polymeric flocculants is a better term. Polymeric flocculants are believed to act by tying together many small particles into a floc that is large enough to settle rapidly. Most attention has been given to obtaining good solids removal with polymeric flocculants but they can also be used to improve filterability of sludge. Unfortunately, the flocculant that gives the best clarity may not be the one that produces the most filterable sludge.

The proper dose of a polymeric flocculant depends critically on the content of colloids of opposite sign in the water as well as on the surface area of the precipitate. Overdosing must be avoided, not only because polymeric flocculants are very expensive but also because an overdose can redisperse the floc. Economical techniques for using polymeric flocculants have not been worked out for systems that change with time such as sewage and mine drainage. There is even evidence that different polymers may be needed at different seasons as the chemical composition of the stream changes. All of these facts make it very difficult to design and estimate costs of equipment and chemicals for dewatering sludges at a new location. Extensive laboratory and even pilot plant studies are necessary to find the best polymer for a given stream and continuous testing is necessary to maintain optimum dosage as flows change (Dean, 1965).

Dewatering

Precipitation and flocculation leaves a relatively clear unpolluted water which may be safely discharged if the salt content is not too high. It also produces a wet sludge that contains 1 to 5% solids. More importantly, 95 to 99% of the sludge is water with a volume that may be as high as 10% of the total flow. The cost of disposing of this sludge is dominated by the cost of handling the water. A one percent sludge contains 99 lbs. of water per pound of solids and this water must be stored or hauled along with the solids. Obviously, anything that can be done to increase the solids content and get rid of the water before disposal of the sludge should be given careful consideration.

The simplest dewatering device is a lagoon in which the solids settle to the bottom and clear water overflows. Lagoons are usually the cheapest way to dispose of sludges--until they fill up (Dean, 1969). Too often lagoons have been designed without thought of eventual disposal of the solids. There has frequently been a hope on the part of the designer that he will be retired before the lagoon fills up and something has to be done about it.

Some precipitates including calcium sulfate settle to a dense mass with a water content low enough so that it can be handled by earth moving equipment and used for landfill. Other sludges including iron and aluminum hydroxides settle to a soft gel that is too weak to support a load and can represent a permanent liability. Similar gels are common in wastes from water treatment plants that use alum as a clarifying agent. One method of dewatering these gels is slow freezing followed by thawing (Doe et al., 1965). Complete freezing is necessary or the unfrozen sludge will interfere with dewatering. Although two water treatment plants in England use mechanical freezing, recent studies sponsored by the FWPCA

have shown that this is not an economical method of dewatering. Natural freezing in thin layers is much more promising in northern regions. The optimum thickness which can be frozen depends, of course, on the climate but is of the order of inches at a time. It should be possible to apply several layers successively on top of previously frozen material during a normal winter in Pennsylvania. In Copenhagen, Denmark, which has a winter no colder than New York City, freezing in shallow layers is used to dewater alum sludges from the Sonderø water treatment plant. After freezing the sludge dries to a hard, friable solid that supports growth of weeds and grasses. Iron hydroxide sludges from mines in England have been dewatered by natural freezing in shallow lagoons or by flooding of level areas.

Centrifuges effectively increase the force of gravity manyfold so that particles will settle in seconds, instead of minutes to hours required in clarifiers and thickeners. Because there is mechanical agitation, centrifuges are relatively poor clarifiers and find their principal application as dewatering devices. The type most suitable for sludges is the horizontal bowl continuous centrifuge (Albertson and Guidi, 1969). A horizontal centrifuge resembles a clarifier with rakes continuously removing the accumulated sludge. The rakes take the form of a scroll that is spun slightly slower than the shell and which works the sedimented solids out one end. The concentrated fraction may contain over 50% solid matter. The action of the scroll inevitably disturbs sedimentation and horizontal centrifuges do not produce a clear effluent. Solids capture varies from 50 to 90% and the solids which escape in the centrate must be removed in some other way. If a single precipitating substance is involved, the centrate containing fine particles is usually returned to the head of the plant for reprocessing. A mixture of calcium sulfate and ferric hydroxide, however, might be separated with only calcium sulfate coming off in the dewatered stream and all the iron being retained in the centrate where it would be continuously recycled. Polymeric flocculants are used in relatively large quantities to improve solids capture in horizontal centrifuges and represent a substantial part of the cost of operation of such equipment.

Vacuum filters of the continuous drum type are the most popular devices for dewatering sludges (Kershaw, 1967). Filtration takes place by suction through a filter cloth that is usually made of synthetic fiber. Colloidal sludges usually yield clear filtrates because the sludge forms its own dense filter medium on the cloth, but this fact also severely limits filtration rates. Flocculant aids are necessary for efficient operation. It is heartening to note that the most common combination of chemicals used as a flocculant aid for filtering sewage sludge is a mixture of ferric sulfate and lime. It is probable that chemical additives may increase filtration rates but they would have to be individually adjusted to the composition of the water being treated.

Brines from demineralizing equipment are especially difficult to dewater because the solid content is all in solution. Total evaporation is economically feasible in this country only in the arid western half where solar evaporation exceeds rainfall. Transport of brines can be expensive. If transport is to be by rail or truck, an economic balance must be struck between the cost of evaporating water and the cost of shipping it. Large quantities of water can be moved most economically by pipeline and the cost does not increase in direct proportion to the volume. Thus Smith (1969) has estimated a cost of $4 per 1000 gallons pumped 100 miles at a flow of 100,000 gallons per day and only 60¢ per 1000 gallons pumped 100 miles when the flow reaches 1 million gallons per day. In some cases it will be less expensive to transport total flow to acceptable receiving waters than it would be to concentrate before shipping. Each case will have to be worked out in detail since transportation costs are so sensitive to geographical location.

Disposal

Sludge that has been dewatered sufficiently to produce a solid residue may be disposed of by dumping in the same places where other mine spoil is deposited. The hitch is, of course, the cost of dewatering to a solid. Some sludges can not be dewatered beyond a thick soup except by evaporation of the water which is a very costly process. The choice of dumps for semisolid sludges is severely limited. In general, some form of a lagoon must be used. The Aberfan disaster in Wales a few years ago, when a mine dump containing slurry collapsed, destroying a village, illustrates the magnitude of the problem which can develop when soft sludges are stored above grade (Engineer, 1966).

Underground storage of semi-solid materials should not pose a problem if abandoned deep workings are available. Low solids sludges will continue to lose water and could contribute to ground water problems. One demonstration in which sludge has been placed in an upper level of a mine has apparently increased drainage from deeper workings to an alarming extent.

Injection wells have been used for acid pickling wastes, and in some cases for thin slurries (Warner, 1965 and 1967). The safety of deep well disposal methods has been questioned (Sheldrick, 1969), and in some cases there is good evidence that deep well injection has caused earthquakes (Healy et al., 1968) and pollution of valuable ground water. The most favorable situation would appear to be reinjection of brine into saline aquifers that have already been partially depleted, as by removal of petroleum or salt. Very careful geological appraisal by independent experts should be employed before a commitment is made to use deep well disposal (Piper, 1969).

The solid constituents of sludges from treated mine drainage, predominantly calcium sulfate and hydrous iron oxides contaminated with unreacted limestone, are all natural soil minerals. With suitable control they can be added to the soil without impairing its properties. Organic sewage sludges have been disposed of in the wet state to pasture and agricultural land for years with substantial benefit to the land (Evans, 1969). A large part of the benefit is not in the recognized fertilizer content, but in the water that is applied during the dry season. If the salt content of the water is not too high, sludges may be disposed of very economically by wet spreading on agricultural or forest land. In this way, the land is used as a low-cost, self-regenerating filter, and the water enters the natural ground waters. Further, neutralization by soil minerals will occur, but, of course, care must be taken to avoid gross runoff or underground channeling to surface streams. FWPCA is to demonstrate this method through a grant to Hi-Hills Ranch and Jones and Laughlin Steel Company.

The rate of application depends both upon the nature of the sludge and the degree of cultivation as well as the nature of the underlying soil minerals. Grasses can grow up through an inch or more of granular material a year, if it is not applied as a dense cake. One lagoon for industrial wastes near Cincinnati receives calcium carbonate and furnace ash. The dewatered sludge has been cultivated and cropped in wheat and corn until the present ground level is several feet above the original grade. Crops are considered good for the area and no deleterious effects have been noted, except that a heavier than normal application of fertilizer is required.

In all land disposal systems great care must be taken to avoid overloading and destruction of the soil-plant interactions by mechanical suffocation. Natural freezing, when present, substantially aids dewatering as has already been noted, and also breaks up coherent sludge cakes permitting penetration by plants in the following season.

The actual quantities which can be disposed of on a given plot of land must therefore be determined by actual experiment. A one-inch layer could probably be tolerated if it were applied in several doses. On one acre, one inch corresponds to more than 100 tons of sludge solids. If we take the figures of Holland et al. as quoted by Hill (1968) for lime neutralization of sludge, one acre an inch thick could take the sludge developed by up to 4 million gallons of drainage each year. More dilute wastes would permit the application of sludge from even greater volumes.

Since additional dewatering takes place on the land, initial concentration is not as critical as for disposal as a solid in dumps. Application to uncultivated land may be by tank, wagon, or sprayer of the Rain Gun type. Sludge can be pumped over a mile in portable irrigation pipe (see also Sanders, 1969). Land that is level or contour cultivated can also receive sludge in irrigation furrows. For any land disposal scheme a storage lagoon will usually be necessary since there will be periods when weather or crop conditions preclude sludge spreading.

Disposal to the ocean may be practical in some cases and the ocean is one of the few acceptable locations for the disposal of brines. Acid wastes have been dumped from bays in charted acid grounds outside New York Harbor for many years. It is possible to design ocean outfalls so that dilute wastewaters will be dispersed in deep waters and not reach the surface (Brooks, 1960). Sea water is a strong buffer with a hardness of about 240 mg/l as $CaCO_3$ and ample dissolved oxygen, so acidity would be neutralized and iron would be precipitated. Care should be taken in placing the outfall where the sediment of hydrous iron oxides would not interfere with useful marine organisms. Surface discharge on the coast or in an estuary would be objectionable in most cases because of unsightly deposits and interference with crustaceans and fish breeding grounds. In some areas long discharge pipes to deep waters off the Continental Shelf may be required. In addition, most mines are located at some distance from the ocean, so pipeline costs would be high.

CONCLUSION

The disposal of pollutants in mine drainage is difficult because they are diluted with so much water. Sale of extracted pollutants is not economical. Acid can be neutralized but sulfates are left in solution. Iron can be precipitated but the precipitate is one of the most difficult to dewater. Ultimate disposal of solids will be to the land, either in dumps or spread thinly on pasture or woodland. Brines too strong to be accepted in surface waters must go to permanent storage or to the ocean. This paper has reviewed available processes for dealing with mine drainage and points out difficulties and advantages associated with them.

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